Characterization of saccharides and associated usage in determining biogenic and biomass burning aerosols in atmospheric fine particulate matter in the North China Plain

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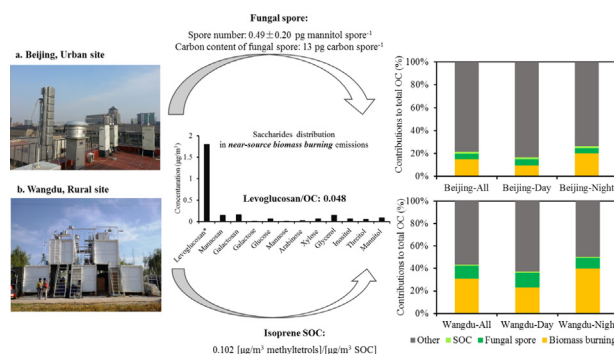[b] Department of Atmospheric Science, Colorado State University, Fort Collins, CO 80523, USA
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HIGHLIGHTS

- Saccharide distributions at rural/urban sites during day-/nighttime were compared.
- Saccharide profiles in PM$_{2.5}$ from near-source biomass burning were investigated.
- Biomass/biogenic sources contributed more OC at rural site than urban site in NCP.
- Contributions of biomass burning were higher at night while fungal spore in the day.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Although biogenic aerosols play important roles in atmospheric processes and climate change, their contributions to atmospheric particulate matter mass have not received much attention, partly due to the difficulty in identifying key aerosol components and due to the often dominant role of anthropogenic emissions. In order to estimate contributions of biogenic and biomass burning organic aerosols to atmospheric particles, fine particulate matter (PM$_{2.5}$) samples were collected simultaneously at an urban and a rural site in the North China Plain (NCP), a region with extensive anthropogenic emissions, during summer 2014. Saccharides, including anhydrosugars, monosaccharides, and sugar alcohols, were quantified. Profiles of saccharides in PM$_{2.5}$ collected at urban and rural sites during the daytime and nighttime, nearby biomass burning, and without significant influence of biomass burning were investigated and compared. Contributions of biomass burning, biogenic aerosol associated with primary biological aerosol particles, and isoprene-derived secondary organic carbon (SOC) to total organic carbon were then estimated based on source-specific saccharide tracers. The results showed that concentrations of nearly all saccharides were higher at the rural site than at the urban site. Levoglucosan was the most abundant saccharide, followed by glycerol and glucose. Mass concentrations of source specific tracers and associated source contribution estimates indicated that the absolute and relative contributions of biomass burning were both much higher compared to fungal spore derived OC and isoprene SOC, with greater contributions observed at the rural site especially during nighttime. Our findings reveal that biogenic and biomass burning sources are non-negligible summertime contributors to atmospheric PM$_{2.5}$ OC mass both at the rural site (up to 50%) and at the urban site (~20%) in the NCP.

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1. Introduction

Saccharides, one of the major classes of water-soluble organic compounds (WSOC) in atmospheric aerosols, are ubiquitous over the continental, marine, and polar regions (Chen et al., 2013; Fu et al., 2012). Atmospheric saccharides usually include anhydrosaccharides (e.g., levoglucosan, galactosan and mannosan), monosaccharides (e.g., glucose, fructose and xylose), disaccharides (e.g., sucrose and trehalose) and saccharide polyols (e.g., arabitol, mannitol and sorbitol) (Li et al., 2016, and references therein). These saccharides in ambient aerosols might originate from numerous sources, such as soil and dust (Jia and Fraser, 2011; Simoneit et al., 2004a), biomass burning relating to wild or prescribed fires and residential biomass combustion, primary biological aerosol particles (PBAPs) (e.g., fungal and fern spores, pollens, algae, fungi, bacteria, and plant debris) (Graham et al., 2003; Jia and Fraser, 2011), and biogenic secondary organic aerosol (SOA) (Holden et al., 2011), which are also major sources of contemporary carbon particles. Given the important roles biogenic aerosols play in public health, atmospheric chemistry and physics, and global climate by serving as cloud condensation nuclei and ice nuclei, as well as their long-range transport, they have received somewhat greater attention in recent years (Christner et al., 2008; Després et al., 2012; Pöschl et al., 2010) than in the past. However, the constituents, concentrations and origins of atmospheric biogenic aerosols are still relatively poorly understood and quantified (Liang et al., 2013a). This is especially true in urban areas, where most attention has been paid to anthropogenic particulate emissions due to the rapid increase in industrialization.

Saccharide compounds in aerosols have been proposed as tracers for tracking sources, processes and transport of biogenic and biomass burning aerosols (Jia et al., 2010; Medeiros and Simoneit, 2007). For example, levoglucosan (LG) and related anhydrosaccharides isomers, produced from the pyrolysis of cellulose and ranking as the most abundant species in biomass burning emissions, have been recognized as a specific molecular marker for biomass burning sources (Engling et al., 2006; Fraser and Lakshmanan, 2000; Simoneit et al., 1999; Sullivan et al., 2014). They are frequently utilized in tracking and estimating biomass burning contributions to atmospheric fine particulate matter all over the world. Arabitol and mannitol are common soluble carbohydrates and storage compounds of fungal spores, and have been proposed as biomarkers for airborne fungal spores (Bauer et al., 2008; Zhang et al., 2010) and used to estimate atmospheric fungal spore abundance and its associated contributions to atmospheric organic aerosols (Bauer et al., 2008; Holden et al., 2011; Liang et al., 2013a, 2017; Zhang et al., 2010). Glucose, sucrose and trehalose have been proposed to be generic marker compounds for fugitive dust from crop fields (Rogge et al., 2007). PBAPs are biologically derived materials such as fungal spores, pollens, bacteria and fragments of plants (Després et al., 2012; Elbert et al., 2007; Jaenicke, 2005). In addition to primary biogenic and biomass burning related sources, oxidation of biogenic volatile organic compound (VOC) emissions to produce SOA has also been suggested to be an important contributor to biogenic fine particulate organic carbon (OC). For example, methyltetrols, including 2-methylthreitol and 2-methylerythritol, are oxidation products of isoprene and have been suggested as tracers of isoprene-derived SOA (Claeys et al., 2004; Kleindienst et al., 2007). However, there are a limited number of studies quantifying the abovementioned biogenic related aerosol contributions to ambient aerosol. Therefore, there is still a significant need to characterize biologically derived PM sources, especially in regions where agricultural and natural sources are greater than anthropogenic sources.

The North China Plain (NCP), situated in the center of northeast China, is one of the most developed and polluted regions in China. It includes two megacities (i.e., Beijing and Tianjin) and three provinces (i.e., Shandong, Hebei, and Henan). NCP represents a region with concentrated extensive anthropogenic emissions, which have caused severe fine particulate pollution, especially under unfavorable meteorological conditions. Several of the top polluted cities in China are located in this region. Meanwhile, the NCP is also one of the major grain production areas in China, comprising approximately 23% of China's cropland area (Zhang et al., 2011) and accounting for 18.6% of the total agricultural area in China (Zhang et al., 2014a). Maize (corn) and wheat are the main grain crops grown in the region. Therefore, biogenic and biomass burning emissions in this region are also considerable due to the extensive agricultural activities (Yan et al., 2017). Although many studies have been conducted on atmospheric aerosols in the NCP region, few have focused on saccharide compounds or biogenic aerosols. Liang et al. (2013a) evaluated fungal spore characteristics in Beijing based on molecular tracer measurements, and then estimated the contribution of fungal spores to organic carbon in ambient aerosols (Liang et al., 2017). Yan et al. (2015) revealed the significance of biomass burning to water-soluble brown carbon based on saccharide compound tracers. Liang et al. (2016) investigated seasonal variations of saccharides in atmospheric particulate matter and further revealed their sources using positive matrix factorization analysis.

In this study, fine particulate matter samples were collected synchronously during daytime and nighttime across the summer wheat harvest season, at an urban site and a rural site in NCP, China. Given the documented roles of saccharides as tracers for biomass burning (Fraser and Lakshmanan, 2000; Simoneit et al., 1999), PBAPs and other biologically derived carbohydrate sources (Bauer et al., 2008; Elbert et al., 2007), saccharide compounds were analyzed. The primary goals of the study were (1) to investigate the abundances and differences between saccharides at urban and rural locations in the NCP, (2) to characterize saccharide profiles during significant biomass burning influence periods and normal periods, and (3) to understand the contributions of biomass burning, as well as PBAPs and secondary biogenic organic aerosol to total atmospheric organic aerosol concentrations based on saccharide biomarkers.

2. Materials and methods

2.1. Sample collection

Ambient fine particulate matter (i.e., particles with aerodynamic diameter less than or equal to 2.5 μm, $PM_{2.5}$) samples were synchronously collected at an urban site in Beijing (BJ) and a rural site in Wangdu (WD), Hebei province from 9 June to 8 July 2014, during the CAREBEIJING-NCP (Campaigns of Air Pollution REsearch in Megacity BEIJING and North China Plain) summer field campaign (see Fig. 1). $PM_{2.5}$ samples were collected on quartz and Teflon filters using one set of high-volume sampler (VFC-$PM_{2.5}$, Thermo Fisher Scientific Co., U.S., with a flow rate of 1.13 m^3/min, quartz filter) and four-channel sampler (TH-16A, Tianhong, China, 16.7 L/min, Teflon filter) simultaneously run at each site during the daytime (from 08:00 to 17:30, local time) and nighttime (from 18:00 to 07:30 next morning), respectively. Altogether, 29 daytime and 28 nighttime samples were collected at the BJ site, and 30 daytime and 30 nighttime samples were collected at the WD site. Quartz filters (Pallflex, Tissuquartz, 2500 QAT-UP, Pall Corp., NY, USA, 8 × 10 in.) were prebaked at 550 °C for 6 h in a muffle furnace and wrapped in pre-baked aluminum foil before sampling. Teflon filters were conditioned and weighed before and after sampling using a microbalance (Mettler Toledo) at constant temperature (20 ± 1 °C) and relative humidity (RH, 40 ± 3%). All samples were stored in triple plastic bags in a refrigerator at −20 °C after sampling until analysis. Field blanks were collected by replicating the environmental exposure to standard field operations but without the sampler pump on, at both sampling sites and using both samplers at the beginning and end of the campaign. All data reported are blank corrected.

The BJ site (39.99°N, 116.31°E) was at the PeKing University urban atmosphere Environment monitoRing Station (PKUERS) located on the rooftop of a teaching building (approximately 20 m above ground level) on the campus of Peking University in northwestern Beijing.
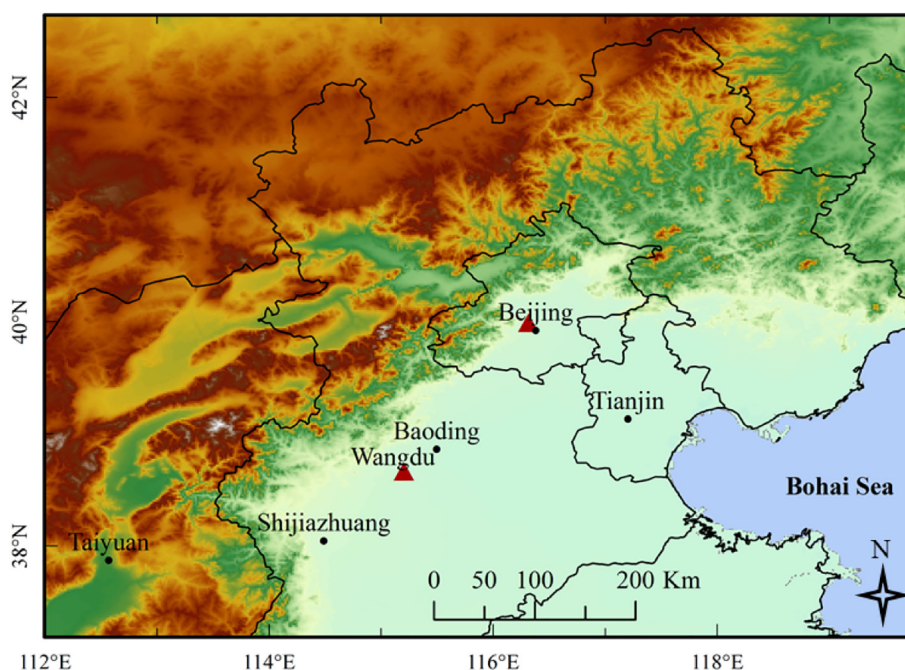
Fig. 1. Location of Beijing and Wangdu in North China Plain. The red triangle indicates the location of two sampling sites.

There were no obvious major emission sources around the BJ site except two major roads (150 m to the east and 200 m to the south). The WD site (38.665°N, 115.204°E) was around 36 km southwest of Baoding city, close to two major industrial cities (i.e., Baoding and Shijiazhuang) in the NCP and surrounded by several coal-fired power plants within 200 km (Liu et al., 2017). The WD site was impacted by agricultural activities such as crop residue burning and fertilization. At the WD site samplers were set up on the top of a two-story stacked container (about 6 m above ground level) placed in a botanical garden, surrounded by farmland, with near-source biomass burning activities during the sampling period due to the summer wheat harvest, but without obvious nearby traffic or major industry emissions. The distance between the BJ and WD sites is approximately 200 km.

2.2. Chemical analysis

Teflon filters collected by the four-channel samplers were extracted in deionized water (DI water, >18 MΩ) with ultra-sonication for 30 min to measure water-soluble inorganic compounds (e.g., K^+, water-soluble potassium) and organic acids (e.g., oxalic acid) by ion chromatography (DIONEX ICS-2500 and ICS-2000, respectively. More details of this method can be found in Guo et al. (2010). In this study, only K^+ was used, with a detection limit of 0.1 mg L^{-1} in the aqueous extract.

One punch (2.25 cm^2) was taken from each Hi-Volume quartz filter sample to analyze for OC and elemental carbon (EC) using a Sunset Laboratory OC/EC analyzer following the National Institute for Occupational Safety and Health (NIOSH) 5040 thermal-optical method (Birch and Cary, 1996). The temperature steps were 250,500, 650, 850 °C in helium and 650, 750, 850, 940 °C in 2% oxygen and 98% helium. The detection limits were 0.6 μgC m^{-3} for OC and 0.2 μgC m^{-3} for EC.

A 47-mm punch of each Hi-Volume quartz filter sample was extracted in 10 mL of DI water (>18 MΩ) with ultra-sonication for 30 min without heating and filtered using a 0.2 μm PTFE membrane filter (Whatman Inc.). Each extract was analyzed for water-soluble organic carbon (WSOC) and saccharides. WSOC was determined using a Sievers Model 800 Turbo Total Organic Carbon (TOC) Analyzer. This analyzer determined WSOC by converting organic carbon in the sample to carbon dioxide using chemical oxidation via reaction with ultraviolet

light and ammonium persulfate. The carbon dioxide formed was measured by conductivity. The increase in conductivity observed was proportional to the amount of organic carbon in the sample. The WSOC detection limit was 0.1 μg C m^{-3}.

The saccharides were determined using high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD). PAD is an electrochemical technique where hydroxyl groups are electroanalytically oxidized on the surface of a gold electrode. A Dionex DX-500 series ion chromatograph with an ED-50 electrochemical detector operating in integrating amperometric mode using waveform A and a GP-50 gradient pump was used. The separation was performed using a Dionex CarboPac PA-1 column, the details of which can be found in Sullivan et al. [2011a, 2011b, 2014]. Saccharides measured in this study included anhydrosugars (e.g., levoglucosan, mannosan and galactosan), monosaccharides (e.g., arabinose, galactose, glucose, mannose and xylose) and alcohols/polyol-sugars (e.g., glycerol, methyltetrols, threitol and mannitol). Here, methyltetrols were the sum of 2-methylthreitol and 2-methylerythritol. The detection limits for individual saccharides were calculated to be less than approximately 0.10 ng m^{-3}.

It can be noted that all carbonaceous species (e.g., OC, EC, WSOC and saccharides) were analyzed with the same quartz filter sample collected by the high-volume sampler. Only K^+ data was from Teflon filter installed on the low-volume four-channel sampler. The choice of filter types for different chemical species is the same as those in the literature due to reasons such as the requirements for mass for chemical analysis and pretreatment before sampling.

3. Results and discussion

3.1. Saccharides at an urban versus rural site

3.1.1. Total saccharides

Concentrations of PM$_{2.5}$ carbonaceous components (e.g., saccharides, OC, EC, and WSOC) measured at the two observation sites during the campaign were summarized and listed in Table 1. The total concentration of the 12 saccharides ($\sum$saccharides) quantified in the atmospheric fine particulate matter accounted for 4.3 ± 1.5%
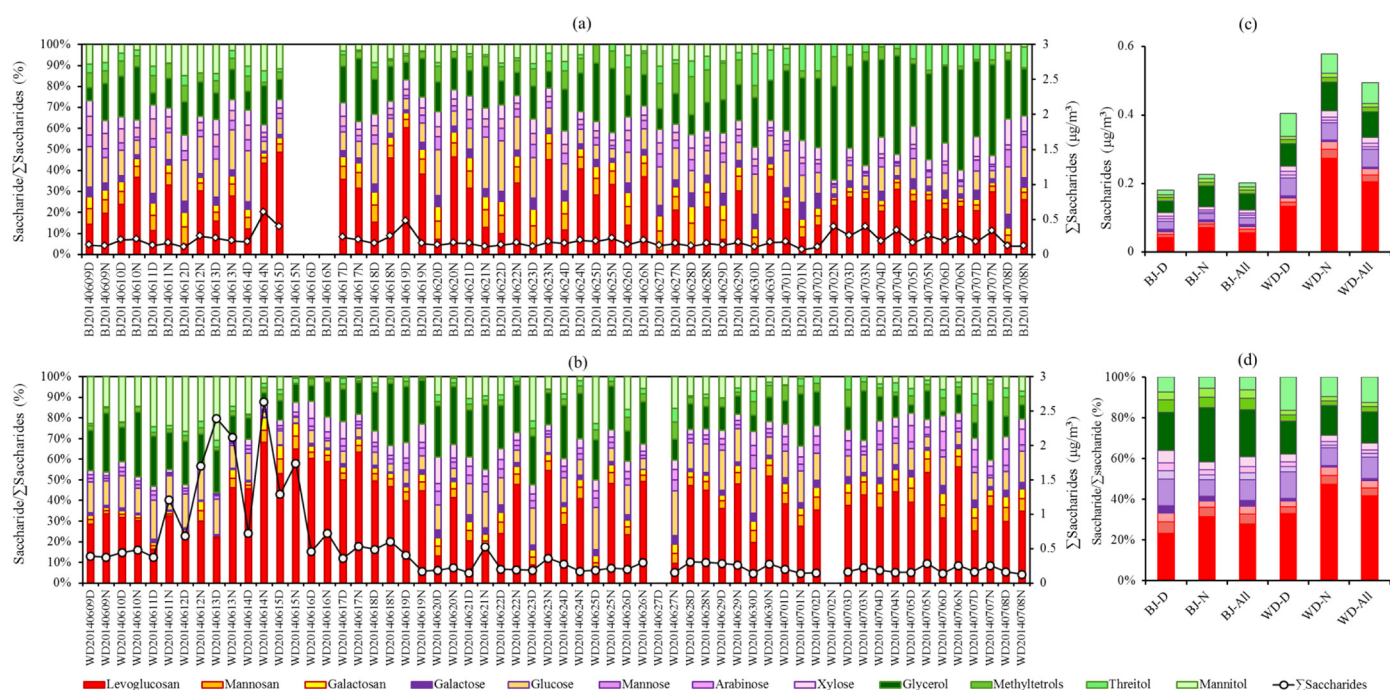
Table 1

Concentrations of the carbonaceous components measured in the fine particulate matter collected at the BJ and WD sites during the sampling campaign.

Compounds (unit)	BJ site (n = 57)					WD site (n = 60)				
	Med.	Ave.	Std.	Min.	Max.	Med.	Ave.	Std.	Min.	Max.
Anhydrosugars (unit: ng/m³)										
Levoglucosan	49.40	56.37	55.48	2.55	289.10	104.28	205.94	304.35	11.60	1803.10
Mannosan	10.93	10.30	3.54	3.30	18.86	11.25	19.80	27.97	5.76	150.38
Galactosan	7.57	7.49	2.51	2.59	15.02	8.53	17.47	28.63	4.99	160.98
Subtotal	69.46	74.16	58.92	11.22	322.98	126.27	243.22	357.95	24.84	2114.46
Monosaccharides (unit: ng/m³)										
Galactose	5.52	5.80	1.23	3.78	8.34	4.92	5.22	1.94	3.25	15.41
Glucose	19.56	21.02	8.26	8.57	45.33	26.98	51.18	70.07	10.48	411.50
Mannose	6.36	6.38	1.99	3.50	13.20	6.89	8.58	5.97	3.22	43.25
Arabinose	5.57	6.25	3.50	1.60	14.14	8.07	10.04	5.73	4.45	34.70
Xylose	8.69	9.98	3.85	5.15	21.38	10.19	16.32	14.62	6.48	82.82
Subtotal	45.99	49.34	14.25	24.88	92.81	63.47	91.25	82.95	32.10	505.37
Sugar alcohols (unit: ng/m³)										
Glycerol	29.33	46.97	43.37	6.95	196.42	45.25	75.58	80.39	3.24	487.97
Methyltetrols	10.10	11.25	8.36	0.03	54.15	9.36	12.87	12.00	2.04	65.27
Threitol	6.12	8.37	8.17	0.00	33.27	5.67	10.47	15.10	0.43	76.27
Mannitol	10.01	12.98	13.10	1.31	76.00	16.19	61.30	124.68	0.92	740.19
Subtotal	60.90	76.15	51.27	30.29	251.43	77.29	152.82	212.97	25.32	1340.71
$\sum$ Saccharides (unit: ng/m³)	171.93	199.65	99.75	66.39	603.97	279.48	487.29	566.94	124.57	2641.35
OC (unit: μgC/m³)	7.23	7.32	2.92	2.37	17.15	8.61	10.75	7.35	3.68	37.37
EC (unit: μgC/m³)	1.14	1.19	0.72	0.10	4.23	1.36	1.59	0.98	0.20	5.36
WSOC (unit: μgC/m³)	4.85	4.99	2.25	1.45	11.30	5.40	6.30	3.44	0.10	19.41
$\sum$ Saccharides/OC (%)	2.63	2.81	0.83	0.97	5.30	3.49	3.90	1.48	1.61	7.51
$\sum$ Saccharides/WSOC (%)	4.27	4.31	1.48	1.29	8.62	5.43	7.07	5.08	2.18	27.52

Note: "Med", "Ave.", "Std.", "Min", and "Max" represent median, average, standard deviation, minimum and maximum values, respectively. And "n" indicated the number of samples.

(range: 1.3%–8.6%) and 7.1 ± 5.1% (range: 2.2%–27.5%) of the WSOC, and 2.8 ± 0.8% (range: 0.97%–5.3%) and 3.9 ± 1.5% (1.6%–7.5%) of the OC at the BJ urban and the WD rural sites, respectively. Concentrations of $\sum$ saccharides were substantially higher at the rural site (range: 125–2641 ng/m³, average: 487 ± 567 ng/m³, and median value: 279 ng/m³) than that at the urban site (range: 66–604 ng/m³, average: 200 ± 100 ng/m³, and median: 172 ng/m³) (see Fig. 2). That is, the

average $\sum$ saccharides concentration at the rural site was about 2.5 times higher than that at the urban site, with the highest $\sum$ saccharides concentration up to 4 times more abundant at the rural site (2.6 μg/m³) compared to the urban site (0.6 μg/m³). It is noted that the average $\sum$ saccharides measured at the BJ urban site during this study period was lower than those reported at the same site in a previous study conducted in the winter and summer of 2013 (354 ± 97 ng/m³ and 380 ±

Fig. 2. Time series of the percent contribution of each saccharide and the $\sum$ saccharides concentrations at (a) the BJ site and (b) the WD site. Sum of (c) $\sum$ saccharides and (d) percent contribution of each saccharide for day (D), night (N), and all samples at the BJ and WD sites.

221 ng/m³, respectively) (Yan et al., 2015). This might be ascribed to variations in the source emissions as well as a frequent washout effect due to rainfall observed during the 2014 measurement period.

Time series of $\sum$ saccharides and variations of associated individual saccharide compounds in $PM_{2.5}$ at the two sampling sites are shown in Figs. 2 and S1. Interestingly, the $\sum$ saccharides concentrations observed at the BJ site were comparable to those at the WD site for a large portion of the sampling period. It seems there were comparable background concentrations of $\sum$ saccharides, around 110 ng/m³ at BJ and 150 ng/m³ at WD, apart from a period from 11 to 18 June. During that time a dramatic increase in the $\sum$ saccharides concentrations (up to 2.6 μg/m³) occurred at the WD site, up to 10 times higher than the concentrations simultaneously observed at BJ. According to the sampling records, there were significant wheat straw burning activities adjacent to the WD site, especially during the period from 11th to 15th June. Hence, the increase of $\sum$ saccharides was primarily attributed to the nearby biomass burning activities. More detailed discussion will be given in Section 3.3.

3.1.2. Saccharide compounds

As shown in Table 1, average concentrations of the quantified anhydrosugars, monosaccharides and alcohols/polyol-sugars (shown in red-, purple-, and green-colored bars in Fig. 2, respectively) were 74 ± 59, 49 ± 14 and 76 ± 51 ng/m³ at the BJ site and 243 ± 358, 91 ± 83, and 153 ± 213 ng/m³ at the WD site, respectively. Similarly, average concentrations of the three categories of saccharides were all higher at the rural than the urban site. However, the saccharides exhibited distinct compositional characteristics at the two sites. At the urban site, anhydrosugars and sugar alcohols accounted for comparable fractions of $\sum$ saccharides (35.0 ± 12.2% and 36.7 ± 10.0%, respectively), higher than the fraction of monosaccharides (28.4 ± 10.6%). By contrast, at the rural site, anhydrosugars accounted for a much larger percentage of $\sum$ saccharides (45.9 ± 15.3%), followed by sugar alcohols (31.3 ± 11.6%) and monosaccharides (22.8 ± 8.2%). Monosaccharides had the lowest levels of the saccharides and anhydrosugars were the most abundant at both the urban and rural sites, while the fraction of anhydrosugars was higher at the rural site. The absolute concentrations of anhydrosugars at the rural site were on average 3 times (up to 16 times) higher than those measured at the urban site in this study, much higher compared to those measured in other studies, such as in the upper Midwest of United States (22.0 ± 13.8 ng/m³, Sullivan et al., 2011a, 2011b) and Chennai in India (127 ± 51.6 ng/m³, Fu et al., 2010), comparable to those at a mountaintop site in Yunnan province, China (216 ± 91.3 ng/m³, Sang et al., 2013) and an urban background and curbside site in Norway (246 and 57 ng/m³, Yttri et al., 2009), but lower than the annual anhydrosugar concentrations in Beijing reported in previous studies (439.0 ± 308.2 ng/m³, Liang et al., 2016) and at a suburban site in January to March in Norway (526 ng/m³, Yttri et al., 2009).

Distinct distributions of individual saccharide species were observed at the urban and rural sites (see Fig. 3). In general, levoglucosan was found to be the most abundant saccharide compound among the individually identified compounds, accounting for 24.3 ± 13.3% (range: 2.0–60%) of the $\sum$ saccharides at the urban site, and 37.7 ± 14.6% (range: 6.3–68.3%) at the rural site. Concentrations of levoglucosan varied from 2.6 to 289 (average: 56 ± 55) ng/m³ at the urban site and 11.6 to 1803 (average: 206 ± 304) ng/m³ at the rural site, higher than those reported in the warm season in Europe (Giannoni et al., 2012), but lower than the maximum levels observed during the cold seasons in Europe due to wood burning for domestic heating (Giannoni et al., 2012), and those from peatland fires and even background samples in Riau, Sumatra, Indonesia (464 ± 183 ng/m³ and 278 ± 155 ng/m³, respectively) (Fujii et al., 2014). The high levoglucosan concentrations at the rural site were primarily ascribed to open field biomass burning during the summer harvest time.

Glycerol is the second most abundant compound at both sites. Glycerol is a reduced sugar primarily produced by fungal metabolism in soils and emitted to the atmosphere as wind-blown dusts (Simoneit et al., 2004b). Additionally, Liang et al. (2013b) and Wang et al. (2011) demonstrated that glycerol in the ambient aerosols in Beijing could be
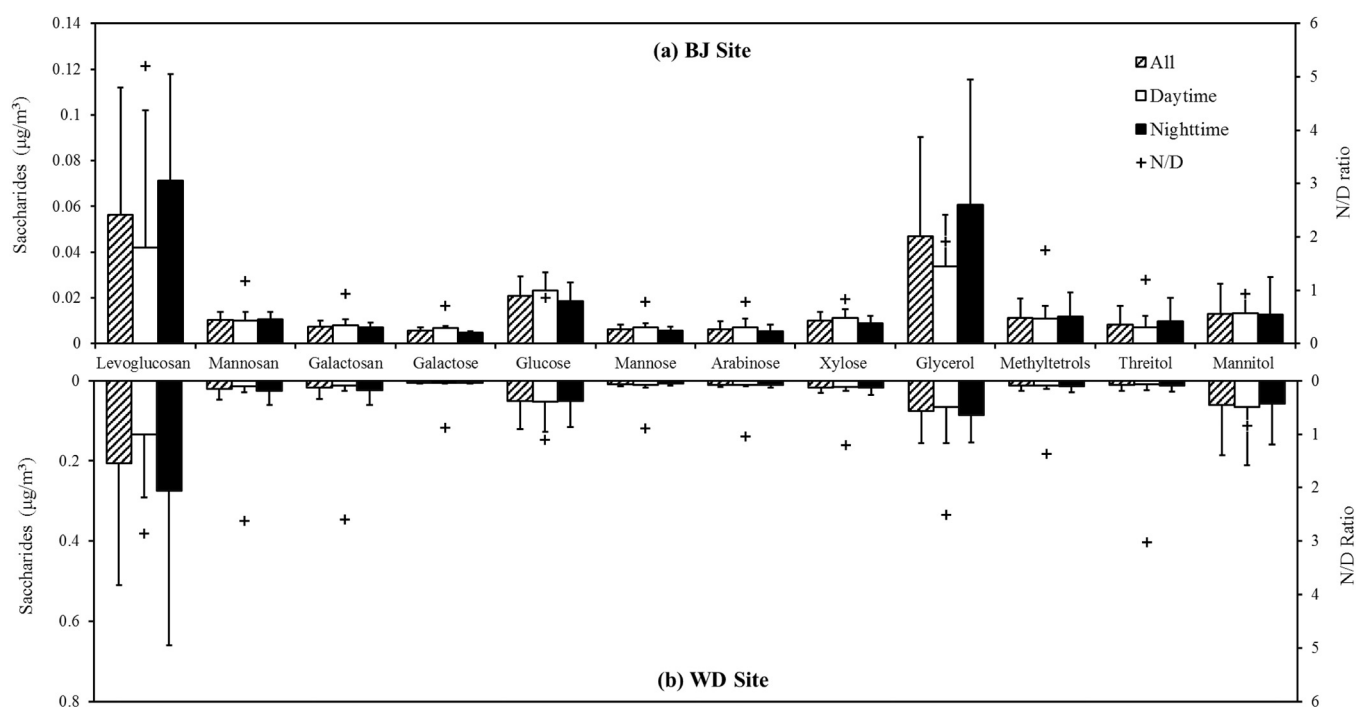

Fig. 3. Distribution of the saccharide compounds at the (a) BJ and (b) WD sites (Note: "all" represents the whole sampling period; "daytime" represents "daytime samples", "nighttime" represents "nighttime samples", and "N/D" represents the average ratio of nighttime concentration to daytime concentration).

mostly attributed to biological sources, and also be influenced by intense biomass burning activities, which can also emit soil materials. For example, Wang et al. (2011) observed sharp increases in glycerol for fresh smoke during wheat straw burning.

Glucose and mannitol also accounted for large proportions of $\sum$ saccharides, with contributions only behind levoglucosan and glycerol at both sites. Previous studies have indicated that saccharide polyols are widespread in fungi, algae, lichens, and higher plants (Lewis and Smith, 1967), as well as thermal stripping during wildfires (Graham et al., 2002; Simoneit et al., 2004b). Mannitol and arabitol have been recognized as major species in fungi and are used as tracers for fungal spores (Bauer et al., 2008; Jia and Fraser, 2011; Yang et al., 2012). Some studies suggested that mannitol, the most abundant saccharide polyol in nature, might also be from marine aerosols (Chen et al., 2013; Lewis and Smith, 1967). Glucose, a common monosaccharide present in vascular plants (Cowie and Hedges, 1984), has broad sources such as pollen, fruits, plant debris and soils (Baker et al., 1998; Fu et al., 2012; Simoneit et al., 2004c; Yttri et al., 2007). Therefore, signatures of saccharides at the two sites indicated that biomass burning and fungal spore activities are important sources of saccharides at both the urban and rural sites.

3.2. Day/nighttime variations

Nighttime $\sum$ saccharides concentrations were typically higher than those during the daytime at both the BJ and WD sites (see Table S1), with the nighttime to daytime (N/D) ratio varying from 0.3 to 3.7 (median value: ~1.3; average value: ~1.4) at both sites. The increase of nighttime $\sum$ saccharides might be attributed to the trapping of saccharide aerosols emitted from the surface under a shallow nocturnal boundary layer. It might also be associated with variations of source emissions, as indicated by differences in N/D ratios between different saccharide compounds (see Fig. 3). Fig. 3 and Table S1 reveal that the average N/D ratios for different saccharide compounds varied from 0.8 to 5.4 at the BJ site and 0.8 to 2.8 at the WD site during the observation period. The absolute contributions of anhydrosugars exhibited an obvious increase at nighttime relative to the daytime at both sites (especially levoglucosan at the BJ site and all three isomers at the WD site), followed by glycerol, threitol and methyltetrols. Nighttime levoglucosan concentrations were observed to be up to 18 times higher than observed during the daytime at the BJ site and up to 11 times higher at the WD site. By contrast, monosaccharide concentrations were higher during the daytime and decreased at night. In general, enhanced nighttime concentrations of sugar alcohols and higher daytime monosaccharide concentrations observed in this study were consistent with the patterns found in the Amazon Basin by Graham et al. (2003). This temporal variability might be associated with the high accumulation and a nocturnal increase in yeasts and other small fungal spores during the nighttime, and higher pollen grains, plant fragments, and fungal spores in the daytime. It could also be evidenced by the distributions of the relative concentrations of saccharide compounds normalized by EC, which is mainly emitted from combustion process and without biogenic source contributions (see Fig. S2).

Despite the relative changes in composition observed during the day vs. night, the average daytime and nighttime saccharide profiles shown in Fig. 3 indicated that atmospheric saccharide concentrations presented similar predominant saccharide compounds (by absolute concentration) during the daytime and nighttime, with levoglucosan, glycerol, and glucose as the predominant compounds at the BJ site and levoglucosan, glycerol, mannitol and glucose at the WD site. As mentioned in Section 3.1.2 and above, glycerol was the second most abundant saccharide at the two sites and significantly higher in concentration during the nighttime, consistent with levoglucosan concentrations, perhaps reflecting parallel emissions from biomass burning activities, especially at the WD site.

A Pearson's correlation test was performed using the Statistical Product and Service Solutions (SPSS, version 16.0) software for the dataset containing ambient concentrations of 12 saccharide compounds collected at both sites during the daytime and nighttime. The results for the BJ site and the WD site are summarized in Tables S2 and S3, respectively. Stronger correlations of levoglucosan with mannosan, galactosan and xylose were found during the nighttime compared to the daytime at both the BJ ($r = 0.63$–0.80, $p < 0.001$) and WD ($r = 0.84$–0.97, $p < 0.001$) sites. Compared to daytime, the approximately 2-fold higher nighttime glycerol concentrations were more correlated with levoglucosan ($r = 0.50$, $p < 0.01$), xylose ($r = 0.61$, $p < 0.001$), threitol ($r = 0.062$, $p < 0.001$) and mannitol ($r = 0.79$, $p < 0.001$) at BJ site, while they were better correlated with mannosan ($r = 0.58$, $p < 0.001$), galactosan ($r = 0.58$, $p < 0.001$), arabinose ($r = 0.55$, $p < 0.01$), and xylose ($r = 0.51$, $p < 0.01$) at WD site, again suggesting possibly different source influences at the rural and urban sites. It is noted that many saccharide concentrations exerted good correlations with each other, with some exceptions (e.g., galactose and mannitol at the WD site). During nighttime, levoglucosan, mannosan, galactosan, arabinose, xylose, methyltetrols, and threitol exhibited strong correlations ($r = 0.76$–0.97, $p < 0.001$). Galactose and glucose did not correlate well with the tracers for biomass burning (e.g., levoglucosan), consistent with there being no obvious emission of galactose and glucose from biomass burning (Medeiors and Simoneit, 2008). By contrast, sugar alcohols (e.g., glycerol, methyltetrols, and threitol) exhibited sometimes stronger correlations with each other ($r = 0.67$–0.96, $p < 0.001$) during daytime compared to nighttime (0.64–0.84, $p < 0.001$).
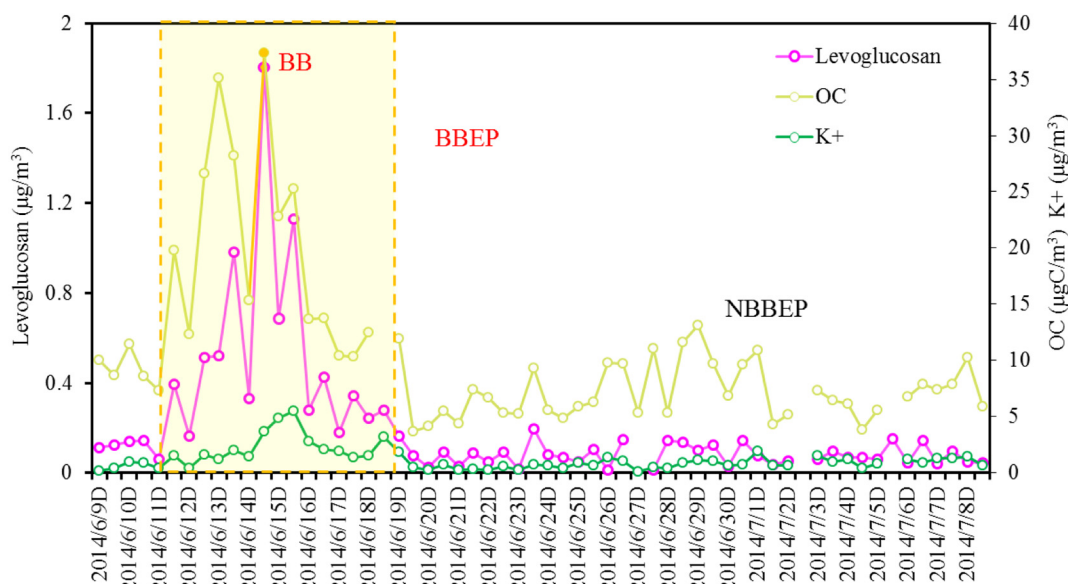
3.3. Characterization of saccharides from near-source biomass burning

As shown in Fig. S1, the nighttime samples collected from 11 to 18 June at the WD site were characterized by a significant increase of $\sum$ saccharides as well as OC, water-soluble K^+ and levoglucosan (see Fig. 4), which could be primarily attributed to field burning of wheat straw during the summer harvest season. This time period was defined as a biomass burning episode (BBEP), and confirmed by MODIS fire hotspot records and 48-h air mass back trajectories (see Fig. S3). The air mass trajectories arriving at the WD site originated from the south and southeast regions, which might also transport polluted biomass burning plumes from regions upwind, in addition to the local biomass burning influence. The sample collected on the night of 14 June, characterized by the highest levoglucosan concentration, was directly influenced by biomass burning activity in the crop field next to the observation site. Therefore, the night of 14 June is identified as an extreme biomass burning event (BB). The remainder of the days (from 20 June to 8 July), which had no obvious biomass burning influence according to the levoglucosan levels, were defined as non-biomass burning episodes (NBBEP).

The average saccharide concentrations and associated relative contributions to $\sum$ saccharides during these different periods are plotted in Fig. 5a–d. The meteorological conditions were similar between the BBEP and NBBEP period at both sites (see Table S4). Obviously, the concentrations of all saccharide compounds observed during the BB and BBEP periods were much higher compared to those observed during the NBBEP period. Anhydrosugars were the predominant components during all three periods at the WD sites. The highest fraction of anhydrosugars in $\sum$ saccharides occurred during the BB period, about 80% of the $\sum$ saccharides, much higher than those during the BBEP ($54 \pm 18\%$) and the NBBEP ($44 \pm 14\%$) periods. Sugar alcohols were the second major category, of which glycerol and mannitol were two relatively strong contributors. Monosaccharides accounted for a lower fraction of $\sum$ saccharides, especially during the BB period ($<5\%$), indicating minimal monosaccharide emissions from biomass burning activities, consistent with previous studies.

Levoglucosan was the predominant saccharide compound during all three periods (BB: 68%; BBEP: 50%; NBBEP: 36%). The concentration of
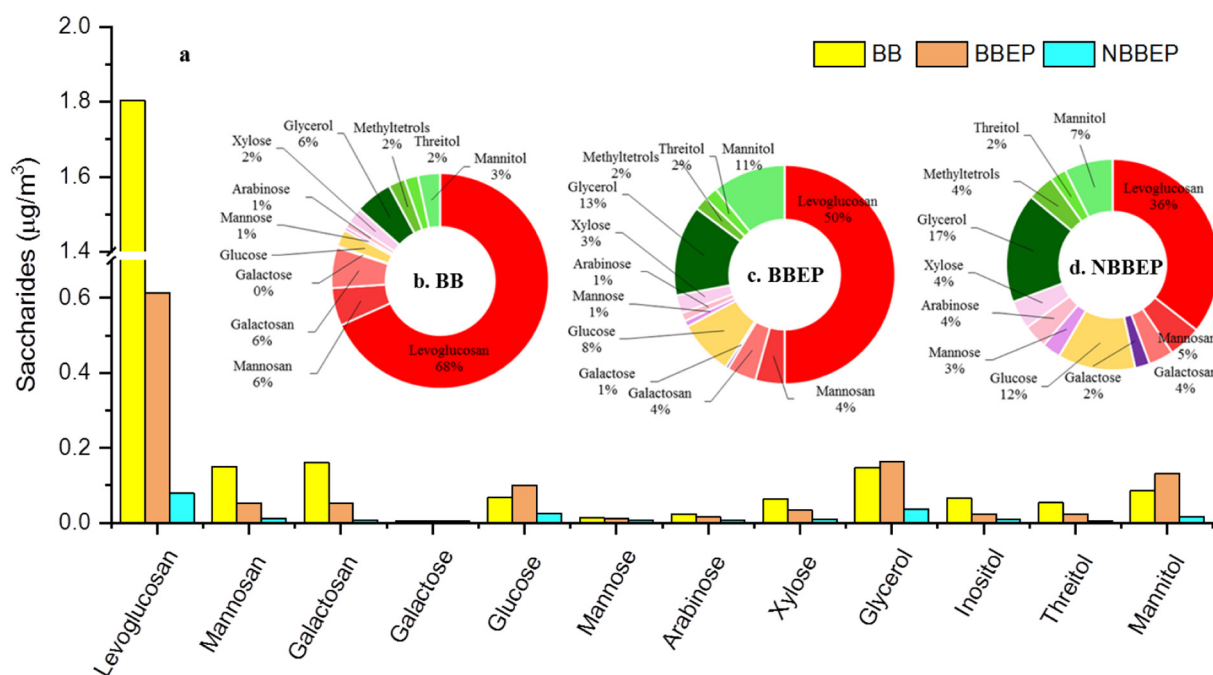
Fig. 4. Time series of OC, levoglucosan and water-soluble K^+ at the WD site. Biomass burning periods were defined as the day with an orange circle representing extremely significant biomass burning in the nearby cropland (BB, 14 June), days labeled within the orange dashed lines representing days with obvious biomass burning influence (BBEP), and days without significant biomass burning influence (NBBEP).

levoglucosan was 1.8 μg/m^3 during the BB period, approximately 20 times higher than the average levoglucosan concentrations during the NBBEP, and similar to the highest levoglucosan values reported during biomass burning episodes in Chengdu, China (Tao et al., 2013). The ratios of levoglucosan (Lev) to other components (e.g., OC, WSOC, EC, and K^+) during the different periods are listed in Table 2. It is noted that the average Lev/OC ratio (μg Levoglucosan/μgC) which has been widely used to estimate biomass burning source contributions, was 0.048 during the BB period. This is higher than those observed in the BBEP and NBBEP periods in this study, in mixed source influenced ambient aerosols in Beijing and Xi'an, China (0.021–0.036, Yan et al., 2015; Zhang et al., 2008, 2014b), and in regional-scale biomass burning

source emissions in Barcelona, Spain (0.015 ± 0.01) (Reche et al., 2012). It is much lower than the value (average: 0.082, within the range of 0.054–0.118) measured in biomass burning source emission tests for three major types of cereal straw (e.g., corn, wheat and rice) burned in residential stoves in China (Zhang et al., 2007). However, the Lev/OC ratio during the BB period in this study was close to the ratios of those measured in near-source rape straw and wheat straw smoke particles or ambient samples during the harvest season, ranging from 0.039 to 0.068 (Engling et al., 2009, 2013; Park et al., 2006; Tao et al., 2013). The difference might be attributed to different fuel types, burning conditions, and/or sampling methods. In addition, it is noted that the nighttime BB sample collected in this study also covered some time period

Fig. 5. (a) Absolute concentrations of the various saccharides for the extreme biomass burning day (BB), biomass burning episode (BBEP), and non-biomass burning episode (NBBEP) at the WD site, and contribution of saccharides during the (b) BB, (c) BBEP, and (d) NBBEP episodes.

Table 2
Ratios of levoglucosan (Lev) to other components during the different periods.

Ratios	This study			Cheng et al. (2013)		Tao et al. (2013)		Urban et al. (2012)
	BB	BBEP	NBBEP	Asian rice straw	Corn straw	Rape straw	Wheat straw	Sugar-cane
Lev/OC	0.048	0.022 ± 0.011	0.011 ± 0.005			0.039	0.068	
Lev/WSOC	0.093	0.045 ± 0.025	0.017 ± 0.009			0.091	0.242	
Lev/EC	0.336	0.213 ± 0.153	0.060 ± 0.026			0.087	1.101	
Lev/K^+	0.494	0.240 ± 0.136	0.113 ± 0.076	0.62 ± 0.32	0.21 ± 0.08	0.103	0.725	0.24

(Note: the units for "Lev/OC", "Lev/WSOC" and "Lev/EC" are μg/μgC)

without obvious biomass burning activities, indicating that it should be representative of a lower limit value for biomass burning activities.

3.4. Sources of saccharides and associated contributions to organic carbon

As previously mentioned, some saccharide compounds are source-specific and can be utilized as tracers to estimate source contributions to atmospheric particulate matter and organic carbon. Here, biomass burning aerosols, PBAPs and secondary organic aerosols were investigated by use of saccharide compounds as tracers and contributions of these sources to total organic carbon were quantitatively estimated. Though applied in many other studies, it should be recognized that the tracer-based method is a rough estimate of source contributions.

3.4.1. Biomass burning aerosols

Biomass burning is a significant source of fine particulate matter during the summertime in north China (Yan et al., 2017). As mentioned, levoglucosan, the most abundant compound in biomass smoke particles, has been recognized as a key tracer of biomass burning emissions (Simoneit et al., 1999). The diagnostic tracer ratio Lev/OC was used to derive the amount of OC originating from primary biomass burning in ambient aerosols. Here, the Lev/OC ratio (0.048) measured in the near-source aerosols influenced by combustion of wheat straw agricultural residues at the WD site was used, in combination with the lev/OC ratios from the ambient samples to obtain a rough estimate of primary biomass burning source contributions to total OC. During the observation period, primary biomass burning contributed around 14.8 ± 9.4% (range: 0.6–43.4%) of the total OC measured at the BJ site, with a daytime average around 9.7 ± 8.8% (range: 0.6–43.4%) and nighttime around 20.2 ± 7.3% (range: 4.4–31.8%), respectively. By contrast, primary biomass burning activities exhibited much higher contributions at the WD site, accounting for 31.3 ± 18.8% of the total OC during the whole observation period, with daytime and nighttime averages of 23.2 ± 13.4% and 39.9 ± 21.2%, respectively.

According to Fig. S3, air masses arriving at the BJ and WD sites might have originated from the regions with extensive biomass burning activities. Therefore, degradation of levoglucosan during atmospheric aging of biomass burning influenced air mass after long-range transport might result in an underestimate of the apportionment of the contribution of primary biomass burning (Hennigan et al., 2010; Holden et al., 2011; Lai et al., 2014; Mochida et al., 2010). Better understanding of the loss of levoglucosan (and other OC components) in smoke aerosol during long-range transport is needed to better constrain future source apportionment estimates.

3.4.2. Primary biological aerosol particles

Due to the rapid increase of industrialization, the majority of current studies have focused on anthropogenic sources in North China, with less attention paid to biogenic emissions. In light of the limited number of studies quantifying the contributions of PBAPs to ambient aerosol, there is an important need to characterize biologically derived PM sources, especially in regions where the role of agricultural and natural sources might be important. Mannitol and arabitol have been proposed as tracers for airborne fungal spores for calculating the contributions of fungal spores to contemporary carbon, because no other emission

sources of these two compounds have been reported (Bauer et al., 2008; Elbert et al., 2007; Zhang et al., 2010).

In this study, mannitol was measured and used for estimating the contribution of PBAPs to organic carbon. The average mannitol concentrations were 12.9 ± 12.5 ng/m³ and 61.5 ± 120 ng/m³ at the BJ and WD sites during the observation period, respectively. These were unexpectedly higher than those reported in fine particles in any previous studies. Yang et al. (2012) indicated that elevated fungal tracer concentrations might be also associated with biomass burning activities. However, poor correlation between mannitol and levoglucosan in this study (see Tables S2 and S3) suggest that biomass burning is not a dominant mannitol source in the study environment. Therefore, total measured mannitol concentrations were used to estimate the contribution of fungal spores to OC (Bauer et al., 2008). The conversion factor for estimating spore numbers from mannitol mass ranged from 0.27 to 0.95 pg (average: 0.49 ± 0.20 pg) mannitol spore^{-1} according to Liang et al. (2013b), and the associated common airborne spore carbon contents (carbon content of fungal spores) ranged from 5.2 to 23 (mean: 13) pg carbon spore^{-1} (Bauer et al., 2002). Using the above range and mean values of these conversion factors, total spore number concentrations during the observation period were 1.4×10^4–4.8×10^4 (average: 2.6×10^4) spores m^{-3}, and spore-derived OC was estimated to range from 176 to 620 ng C/m³ with an average of 342 ng C/m³ at the BJ site, and 6.5×10^4–23×10^4 (average: 12.7×10^4) spore m^{-3} and 853–3002 (average: 1654) ng C/m³ at the WD site. The estimated spore-derived OC is 0.6–11.8% (mean: 4.8 ± 2.9%) and 0.2–55.9% (average: 11.3 ± 12.5%) of the observed OC at the BJ and WD sites, respectively, both much lower compared to estimates from a tropical rainforest by Zhang et al. (2015). The higher contribution of fungal spores to OC at the rural site compared to the urban site, is consistent with the findings by Liang et al. (2017). These results suggest fungi comprise a non-negligible source of carbonaceous aerosol at both sites.

3.4.3. Secondary organic aerosols

Another important class of biogenic organic aerosol can come from secondary organic aerosol. Methyltetrols, including 2-methylthreitol and 2-methylerythritol, are oxidation products of isoprene, and have been suggested as tracers for isoprene-derived SOA to estimate the amount of secondary organic carbon (SOC) present as a result of isoprene oxidation.

During the observation period, the average concentration of 2-methyltetrols measured at the BJ site was 11 ± 8 ng/m³, ranging from 0.029 to 54 ng/m³, lower than the highest summertime 2-methyltetrols concentrations (72.5 ng/m³) observed by Liang et al. (2012). Daytime 2-methyltetrol concentrations at the BJ site were 10.8 ± 5.6 ng/m³, with a range of 0.65–23.7 ng/m³, while the nighttime 2-methyltetrol concentrations varied from 0.029 to 54.2 ng/m³, with an average value of 11.7 ± 10.6 ng/m³. The average 2-methyltetrol concentration measured at the WD site was 12.6 ± 11.7 ng/m³ (range: 2–65.3 ng/m³), with an average daytime value of 12.0 ± 8.2 (3.9–38.8 ng/m³) and nighttime value of 13.4 ± 15.1 ng/m³ (range: 2–65 ng/m³). A ratio of 0.102 [μg/m³ methyltetrols]/[μg/m³ SOC], based on chamber studies reported by Kleindienst et al. (2007), was used to estimate the amount of secondary organic carbon (SOC) present in each sample as a result of isoprene oxidation (Holden et al., 2011).

The estimated 2-methyltetrol derived SOC was 108 ± 80 ng/m³ (range: 0–531 ng/m³), contributing $1.6 \pm 1.2\%$ of the total OC at the BJ site during the observation period, with comparable 2-methyltetrol derived SOC during the nighttime (115 ± 104 ng/m³, $1.7 \pm 1.3\%$ of the total OC) and daytime (106 ± 55, 6–233 ng/m³, $1.7 \pm 1.1\%$ of the total OC). By contrast, the estimated isoprene SOC concentrations were slightly higher at the WD site with an average of 124 ± 114 ng/m³, but accounting for a lower fraction of total OC ($1.1 \pm 0.5\%$). The daytime (117 ± 80 ng/m³, $1.2 \pm 0.4\%$ of the total OC) and nighttime (131 ± 148 ng/m³, $1.1 \pm 0.5\%$ of the total OC) contributions of isoprene SOC at the WD site were also comparable. However, it should be noted that, uncertainties in the SOA-tracer based method might be induced from the limited molecular organic tracers and the uncertainty in the conversion factors, and the contributions of isoprene SOC estimated here might be underestimated (Ding et al., 2016).

3.4.4. Contributions of biomass/biogenic related organic aerosols

Fig. 6 shows average concentrations of source-specific tracers (e.g., levoglucosan, mannitol, 2-methyltetrols, see Fig. 6a), and absolute and relative contributions of the different sub-categories of OC from biomass burning (Fig. 6b), fungal spore derived OC (Fig. 6c), and isoprene SOC (Fig. 6d) to total OC at the BJ and WD sites during daytime and nighttime. From the aspect of absolute OC concentrations, the different sources ranked from high to low as biomass burning > fungal spores > isoprene SOC at both sites, with OC concentrations from all three biomass/biogenic related sources higher at the rural site than at the urban site, and with higher biomass burning OC during nighttime and higher fungal spore OC during daytime.
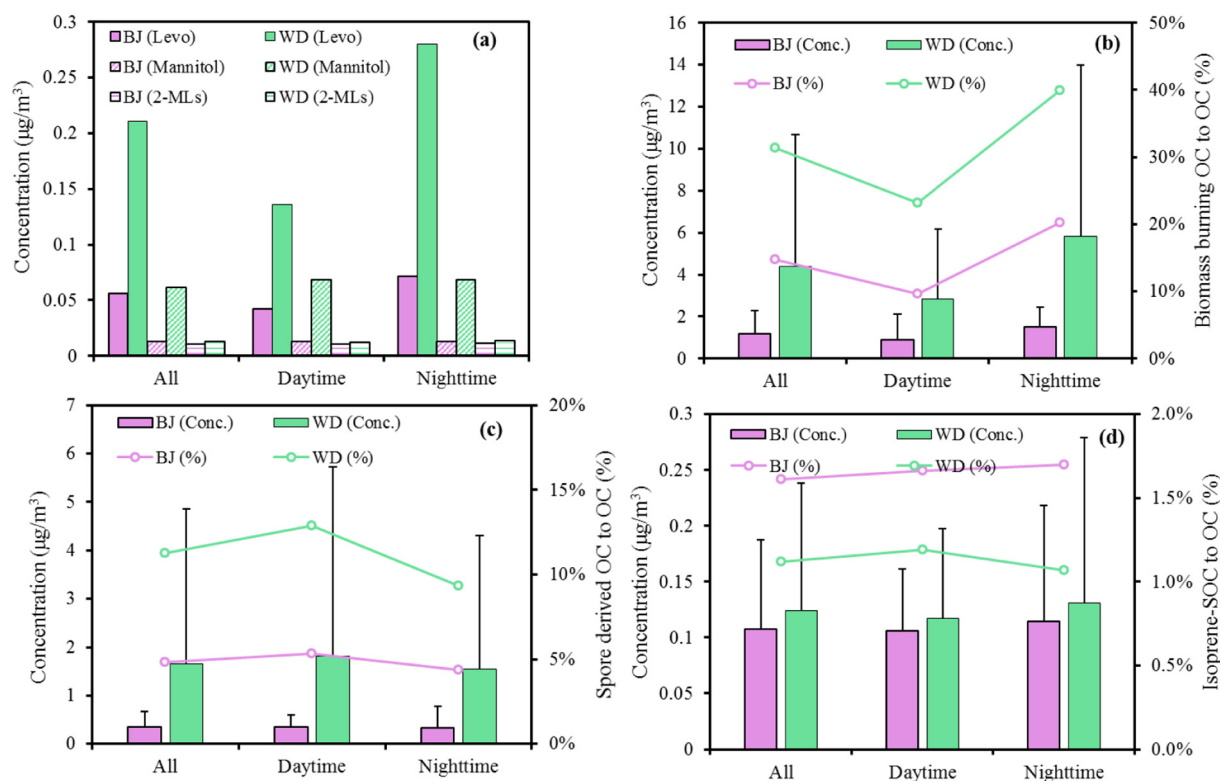
With respect to relative source contributions, similarly, biomass burning accounted for the largest OC contributions, followed by fungal spores and isoprene SOC at both sites. Together, the three biomass/biogenic related sources on average contributed approximately 21% and 44% of the daily total OC at the BJ and WD sites, respectively (see Fig. 7). The finding of higher biomass/biogenic source contributions to

OC at the rural site and larger anthropogenic source contributions at the urban site is not surprising. Interestingly, the total biomass/biogenic source contributions were found to be higher during nighttime than daytime at the rural and urban locations (nighttime vs. daytime: 26% vs. 17% at the BJ site, and 50% vs. 37% at the WD site, respectively). This might reflect, in part, decreased human activities (e.g., industrial and traffic activities) at night. Compared to the rural site, the urban site exhibited relatively lower biomass burning (urban vs. rural: $15 \pm 9\%$ vs. $31 \pm 19\%$) and fungal spore (urban vs. rural: $4.8 \pm 2.9\%$ vs. $11.3 \pm 12.5\%$) source contributions, but similar to slightly higher isoprene SOC contributions (urban vs. rural: $1.6 \pm 1.2\%$ vs. $1.1 \pm 0.5\%$). Such a pattern could result from higher oxidant concentrations in more polluted environments.

Relative contributions of primary biomass burning sources to OC were higher at nighttime compared to daytime, accounting for 20% and 40% of total OC during nighttime at the urban and rural sites, respectively. By contrast, fungal spore derived OC exhibited slightly higher contributions during the daytime compared to nighttime, consistent with the source tracers. Isoprene SOC exhibited comparable contributions during the daytime and nighttime at both sites.

4. Conclusions

Profiles of 12 saccharides in PM₂.₅ at an urban and rural site in NCP, China were quantified and compared during the daytime and nighttime in the summer in periods with and without biomass burning influence. Some similarities were observed in the saccharide profiles and source distributions at the rural and urban sites. Levoglucosan was found to be the predominant saccharide compound, with average fractions in total saccharides of $24.3 \pm 13.3\%$ at the urban site and $37.7 \pm 14.6\%$ at the rural site in ambient samples, ~50% in samples significantly influenced by biomass burning activities, and ~70% in near-source biomass burning emissions. Biomass burning was the most abundant contemporary carbon source in this region, with contributions significantly higher

Fig. 6. Average concentrations of source-specific tracers (a) and contributions of the different sub-categories of OC to total OC: (b) biomass burning, (c) fungal spores and (d) secondary organic carbon during the whole (All), daytime and nighttime sampling periods at both the BJ and WD sites, respectively (Note: "Levo", "2-MLs", and "Conc." represents "levoglucosan", "2-methyltetrols", and "Concentration" respectively).
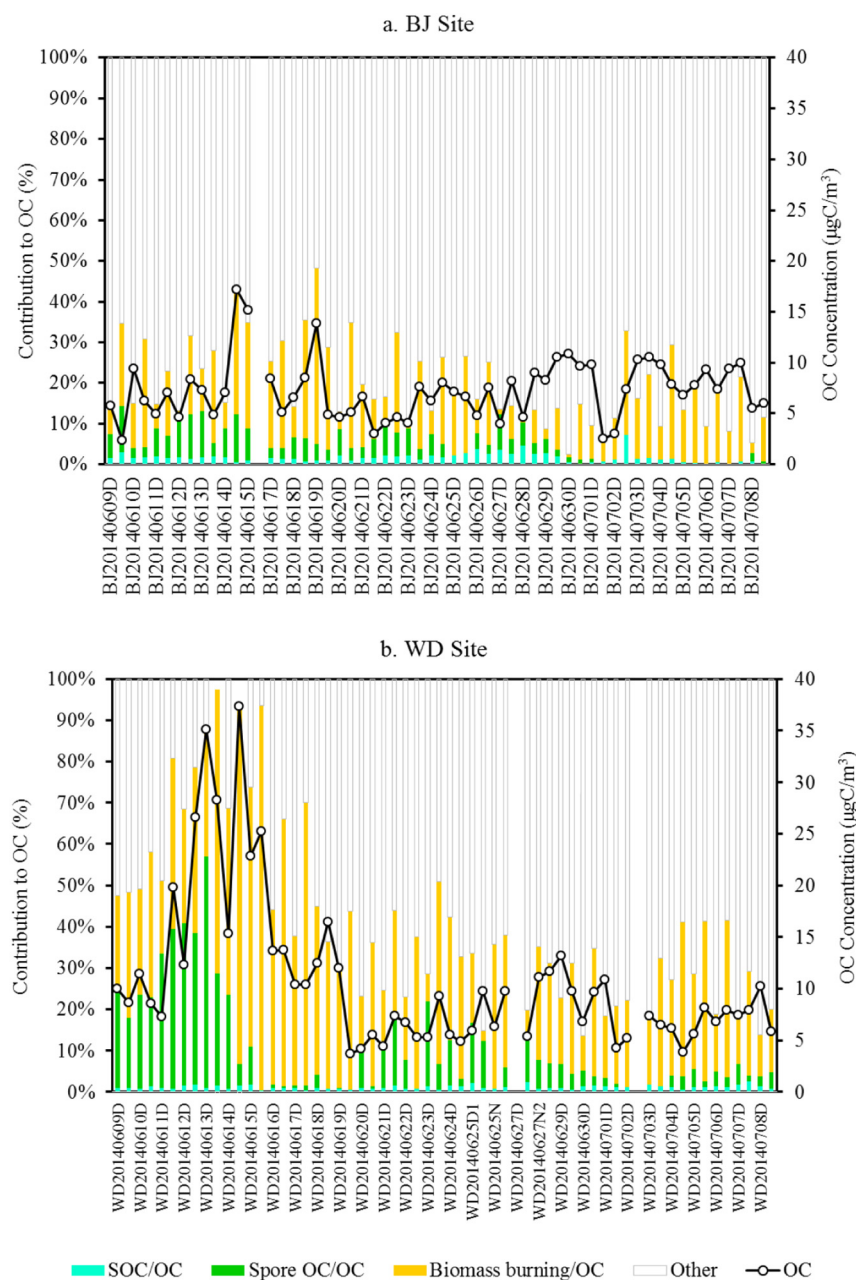
Fig. 7. Time series of the contributions by different sub-categories of OC to total OC along with the absolute OC concentration during the observation period at the (a) BJ and (b) WD sites.

during nighttime, especially at the rural site, indicating extensive biomass burning activities occurred in the evening. By contrast, PBAPs exhibited stronger contributions during the daytime than at night, acting as the second largest contributor to contemporary carbon after biomass burning. Isoprene SOC represented the lowest fraction of contemporary carbon, with comparable contributions during daytime and nighttime. Taken together, contemporary carbon was a non-negligible fraction of total OC in both a rural and urban area in the North China Plain. Contributions of biomass burning and biogenic sources were more significant at the rural site, while contributions of anthropogenic sources were relatively more significant at the urban site.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.09.325.

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